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64 Process for producing ethylene copolymer.

57 In a process for producing an ethylene copolymer by copolymerizing ethylene with an  $\alpha$ -olefin or copolymerizing ethylene with an  $\alpha$ -olefin and a non-conjugated diene in the presence of a Ziegler-Natta catalyst comprising an organoaluminum compound and a compound of a transition metal belonging to Group IV or V of the periodic table or comprising these and a catalyst-activating agent, in a polymerization medium which is substantially incapable of dissolving the resulting ethylene copolymer, and thereby producing a rubberlike ethylene copolymer in particulate form, the improvement which comprises adding to the polymerization reaction system, as adhesion-preventing agent, an alkali metal salt of a sulfocarboxylic acid dialkyl ester or a composition comprising (a) a polysulfone copolymer of sulfur dioxide and an olefin compound, (b) a polyamine comprising a reaction product of epichlorohydrin with an N-aliphatic hydrocarbylalkylene-diamine, and (c) an oil-soluble sulfonic acid.

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## PROCESS FOR PRODUCING ETHYLENE COPOLYMER

### 1 BACKGROUND OF THE INVENTION

#### FIELD OF THE INVENTION

This invention relates to a process for producing a copolymer of ethylene and  $\alpha$ -olefin or a copolymer of  
5 ethylene, an  $\alpha$ -olefin and a non-conjugated diene.

#### DESCRIPTION OF THE PRIOR ART

There is well known a process for producing a copolymer of ethylene and  $\alpha$ -olefin or ethylene, an  $\alpha$ -olefin and a non-conjugated diene (hereinafter referred  
10 to as "ethylene copolymer") by using a so-called Ziegler-Natta catalyst comprising a combination of a compound of a transition metal belonging to Group IV or V of the periodic table and an organoaluminium compound. As the production process, there are known a solution polymeriz-  
15 ation method comprising conducting polymerization in a solvent capable of dissolving the resulting copolymer, or a slurry polymerization method comprising conducting polymerization in a polymerization medium substantially incapable of dissolving the resulting copolymer, and  
20 dispersing a particulate polymer into the polymerization medium. Among these production processes, the slurry polymerization method is widely used because it is advantageous as compared with the solution polymerization method in that the viscosity of solution is low, that stirring

1 and transfer are easy, and that separation of the polymer  
from the polymerization medium is easy.

However, according to the slurry polymerization  
method, the resulting polymer particles adhere to agit-  
5 ing blades, reactor walls, pipes for transfer or the  
like, and mutual adhesion of the polymer particles also  
occurs because in particular, ethylene copolymers have  
adhesiveness. In the case of the ethylene copolymers,  
this adhesion becomes a particularly serious problem.

10 In order to prevent such mutual adhesion of  
the polymer particles, adhesion of the polymer particles  
to reactor walls or agitating blades, and the like, there  
has been proposed a method in which polymerization reaction  
is conducted at a relatively low temperature of  $-80^{\circ}\text{C}$   
15 to  $30^{\circ}\text{C}$  (Japanese Patent Publication No. 10,491/61).  
However, in spite of the procedure at such a low temper-  
ature, there has not yet effectively been prevented  
mutual adhesion of the polymer particles, their adhesion  
to reactor walls or agitating blades, and the like.

## 20 SUMMARY OF THE INVENTION

In producing an ethylene copolymer by such a  
slurry polymerization method, the present inventors have  
investigated a process for producing an ethylene copolymer  
efficiently by lowering the above-mentioned defects and  
25 preventing mutual adhesion of the polymer particles,  
their adhesion to reactor walls or agitating blades, and  
the like, and have consequently found that the purpose

1 described above can be achieved by the presence of a special adhesion-preventing agent in a polymerization reaction system, whereby this invention has been accomplished.

5 The object of this invention is to provide a process for producing an ethylene copolymer effectively.

According to this invention, there is provided a process for producing an ethylene copolymer by copolymerizing ethylene with an  $\alpha$ -olefin or copolymerizing ethylene with an  $\alpha$ -olefin and a non-conjugated diene in the presence of a Ziegler-Natta catalyst comprising an organoaluminum compound and a compound of a transition metal belonging to Group IV or V of the periodic table or comprising these and a catalyst-activating agent, in a polymerization medium which is substantially incapable of dissolving the resulting ethylene copolymer, and thereby producing a rubberlike ethylene copolymer in particulate form, which is characterized by adding to the polymerization reaction system, as adhesion-preventing agent, an alkali metal salt of a sulfocarboxylic acid dialkyl ester or a composition comprising (a) a polysulfone copolymer of sulfur dioxide and an olefin compound, (b) a polyamine comprising a product of reaction of epichlorohydrin with an N-aliphatic hydrocarbylalkylenediamine, and (c) an oil-soluble sulfonic acid.

#### DETAILED DESCRIPTION OF THE INVENTION

As the  $\alpha$ -olefin used in this invention, there are

1 exemplified propylene, 1-butene, 4-methyl-1-pentene,  
1-hexene, etc.

As the non-conjugated diene, there are exemplified  
1,4-hexadiene, dicyclopentadiene, methyldicyclopentadiene,  
5 vinylnorbornene, 5-ethylidene-2-norbornene, isopropenyl-  
norbornene, etc.

As the polymerization medium which is substantial-  
ly incapable of dissolving the ethylene copolymer, there  
are exemplified propylene, propane, 1-butene, butane,  
10 methylene chloride, ethylene chloride, ethyl chloride,  
etc. These are used alone or as a mixture thereof. The  
above-mentioned polymerization medium becomes a reaction  
component in this invention in some cases, and in this  
case, it is used in an amount larger than the amount  
15 consumed for the reaction and the surplus medium acts as  
solvent.

The composition of the ethylene copolymer can  
be changed over a wide range, but when the ethylene  
content becomes high, a partly crystalline polymer is  
20 produced, and hence for obtaining a rubberlike copolymer,  
it is preferable to set the starting monomer ratio so that  
the ethylene content of the ethylene copolymer is 20 to  
90% by weight, preferably 30 to 86% by weight.

As the catalyst for polymerization, there is used  
25 a so-called Ziegler-Natta catalyst which gives a heretofore  
well-known rubberlike ethylene copolymer. This catalyst  
comprises an organoaluminum compound and a compound of a  
transition metal belonging to Group IV or V of the periodic

1 table, and the combination of these can easily be selected  
by those skilled in the art. Further, it is also possible  
to co-use a catalyst-activating agent such as an ester  
of halogenated carboxylic acid, a halogenated ketone or  
5 the like, and a catalyst-modifying agent such as a ketone,  
an ester, an alcohol or the like.

Here, the organoaluminum compound is a compound  
represented by the general formula  $R'_n AlX_{3-n}$  (wherein  $R'$   
is a hydrocarbon group having 1 to 20 carbon atoms,  $X$  is  
10 a halogen atom or an alkoxyl group, and  $n$  is a number  
satisfying  $1 \leq n \leq 3$ ), for example, a compound represented  
by the formula  $R'_3 Al$ ,  $R'_2 AlX$ ,  $R' AlX_2$ ,  $R'_{1.5} AlX_{1.5}$  or the  
like, and these compounds are used alone or as a mixture  
thereof. Concrete examples of these compounds include  
15 triethylaluminum, triisopropylaluminum, triisobutylaluminum,  
trihexylaluminum, diethylaluminum chloride, diethylaluminum  
bromide, diisobutylaluminum chloride, diisobutylaluminum  
bromide, ethylaluminum sesquichloride, isobutylaluminum  
sesquichloride, ethylaluminum dichloride, isobutylaluminum  
20 chloride and the like.

As the compound of a transition metal belonging  
to Group IV or V of the periodic table, vanadium compounds,  
titanium compounds and the like are preferred. As the  
vanadium compounds, there are exemplified compounds  
25 represented by the general formula  $VX_4$ ,  $VOX_3$  or  $VO(OR')_n X_{3-n}$   
wherein  $R'$ ,  $X$  and  $n$  have the same meanings as defined  
above. Concrete examples of these compounds include  
vanadium tetrachloride, vanadium tetrabromide, vanadium

1 oxytrichloride, vanadic acid triethoxide, vanadic acid diethoxychloride, vanadic acid ethoxydichloride, vanadic acid tributoxide, vanadic acid dibutoxychloride, vanadic acid butoxydichloride, vanadium triacetylacetonato, etc.

5 As the titanium compounds, there are exemplified titanium tetrachloride, titanium trichloride, titanium trichloride supported on a magnesium compound, silica or the like.

These can be used alone or as a mixture thereof.

Further, as the catalyst-activating agent,

10 there are used esters of halogenated carboxylic acids, halogenated ketones, halogenated hydrocarbons, etc.

Concrete examples of these compounds include methyl trichloroacetate, butyl perchlorocrotonate, butyl 2,3,4,4-tetrachloro-3-butenate, ester of trichloroacetic acid and  
15 ethyl cellosolve, hexachloroacetone, perchlorobutadiene, etc.

As to the polymerization condition, it is preferable to conduct the polymerization at a temperature lower than that of conventional polymerization conditions  
20 of olefins (e.g., at 40° to 120°C, at atmospheric pressure to 100 kg/cm<sup>2</sup>).

When the polymerization reaction is conducted at a high temperature, adhesion of the resulting copolymer particles occurs. The polymerization at an extremely  
25 low temperature causes a decrease of the polymerization reaction rate, requires a high energy for removing heat of polymerization to maintain the system at a low temperature, and hence is not preferable. Therefore, the

1 polymerization reaction is conducted preferably between  
-40°C and 60°C, more preferably between -30°C and 40°C.

The pressure is atmospheric pressure to  
100 kg/cm<sup>2</sup>, and the polymerization reaction is conducted  
5 in the presence or absence of a chain transfer agent.

As the alkali metal salt of a sulfocarboxylic  
acid dialkyl ester which is one of the adhesion-preventing  
agents used in this invention, alkali metal salts of  
dialkyl sulfosuccinates are preferred, and more concretely,  
10 alkali metal salts of dioctyl sulfosuccinate or dihexyl  
sulfosuccinate are exemplified. As the alkali metal  
salts, sodium salts or potassium salts are preferred.

The composition comprising (a) a polysulfone  
copolymer of sulfur dioxide and an olefin compound, (b) a  
15 polyamine comprising a reaction product of epichlorohydrin  
with an N-aliphatic hydrocarbylalkylenediamine, and (c) an  
oil-soluble sulfonic acid, which is the other adhesion-  
preventing agent, contains benzene, toluene, xylene,  
cyclohexane, fuel oil or the like or a mixture thereof  
20 as solvent, and preferably comprises 5 to 20% by weight  
of the polysulfone copolymer, 5 to 20% by weight of the  
polyamine, 5 to 10% by weight of the oil-soluble sulfonic  
acid and 85 to 50% by weight of the solvent. Further, as  
the polysulfone copolymer, 1-decenepolysulfone consisting  
25 of sulfur dioxide and 1-decene and having an intrinsic  
viscosity of 0.04 to 0.08 (30°C, in toluene, 0.5% by  
weight solution) is preferred. As the polyamine, a  
reaction product of N-talo-1,3-diaminopropane with



1 epichlorohydrin in a molar ratio of 1:1.5 is preferred.  
As the oil-soluble sulfonic acid, dodecylbenzenesulfonic  
acid is preferred.

5 The above-mentioned adhesion-preventing agent  
used in this invention brings about a sufficient effect  
even when added in a very small amount of usually 5 to  
100 ppm, more preferably 10 to 50 ppm based on the  
polymerization medium introduced into a reactor.

10 The polymerization reaction can be conducted  
by a batchwise or continuous operation. As to addition  
of the adhesion-preventing agent, in the case of the  
batchwise operation, said agent is added in one portion  
to a reaction vessel before the beginning of the poly-  
merization, and in the case of the continuous operation,  
15 it is preferable to supply said agent to a reaction vessel  
continuously together with the polymerization medium.  
The adhesion-preventing agents described above can be  
used alone or as a mixture thereof.

20 Thus, according to the process of this invention,  
the polymerization reaction is not inhibited substantial-  
ly, and mutual adhesion of polymer particles or adhesion  
of polymer particles to vessel walls, agitating blades or  
the like is reduced or prevented, so that an ethylene  
copolymer can be efficiently produced.

25 This invention is explained below in more detail  
by way of Examples, but the invention is not limited  
thereto.

1 EXAMPLE 1

In a 1.5-liter autoclave made of stainless steel were placed 400 g of propylene, 50 g of ethylene and 18 mg (40 ppm) of sodium dioctyl sulfosuccinate, and cooled to 0°C, after which 1.0 mmol of ethylaluminum sesquichloride and 0.1 mmol of vanadium oxytrichloride were continuously added. The temperature inside the autoclave was controlled at 0°C. The ratio between un-  
reacted ethylene and propylene in the reactor was controlled  
so that the ratio of them is kept at constant by feeding  
27 g of ethylene continuously to the reactor.

The ethylene-propylene copolymer produced by the copolymerization reaction had suspended as particles in the polymerization medium (propylene). After completion  
of the reaction, the polymerization was stopped by adding  
a small amount of methanol in the reactor, and the  
particulate copolymer was separated from the polymerization  
medium by filtration. The copolymer thus obtained was  
good rubberlike particles having a particle size of about  
2 mm. There was observed no adhesion of copolymer  
particles to the inside of polymerization vessel or  
agitating blades.

Thus, 43 g of the copolymer was obtained. The  
ethylene content of the copolymer was 68% by weight as  
determined by infrared absorption spectrum.

COMPARATIVE EXAMPLE 1

The same procedures as in Example 1 were repeated,

1 except that no sodium dioctyl sulfosuccinate was added.  
In this copolymerization, stirring by a stirrer became  
impossible 10 minutes after the copolymerization was  
started. After the polymerization was stopped by addition  
5 of a small amount of methanol, the same procedure as in  
Example 1 was conducted, but the copolymer thus obtained  
was not particulate but in the form of a large mass  
adhering to agitating blades. The ethylene content of  
this rubberlike copolymer was 66% by weight, and its  
10 yield was 16 g.

#### EXAMPLE 2

Copolymerization was conducted in the same manner  
as in Example 1, except that as an adhesion-preventing  
agent, the sodium dioctyl sulfosuccinate was replaced by  
15 5 mg (11 ppm) of Stadis 450 [a composition consisting of  
a toluene solution (toluene; 66% by weight) containing  
13.3% by weight of a 1:1 copolymer of 1-decene and sulfur  
dioxide having an intrinsic viscosity of 0.05, 13.8% by  
weight of a reaction product of N-talo-1,3-diaminopropane  
20 with epichlorohydrin in a molar ratio of 1:1.5 and 7.4%  
by weight of docecylbenzenesulfonic acid, manufactured  
by E.I. du Pont de Nemours & Co.]. After-treatment was  
carried out in the same manner as in Example 1 to obtain  
45 g of a good rubberlike particulate copolymer having a  
25 particle size of about 2 mm. The ethylene content of  
the copolymer thus obtained was 30% by weight. In this  
reaction, there was observed no adhesion of copolymer

- 1 particles to the inside of polymerization vessel or agitating blades.

### EXAMPLE 3

Into the same reactor as used in Example 1 were  
5 introduced 400 g of propylene and 30 g of ethylene, after  
which 6.5 mg (15 ppm) of sodium dioctyl sulfosuccinate  
was added, and the resulting mixture was maintained at  
5°C. Hydrogen was added as molecular weight regulator  
at a partial pressure of 5 kg/cm<sup>2</sup>, and the copolymerization  
10 was conducted by continuously supplying 1.0 mmol of  
ethylaluminum sesquichloride, 0.02 mmol of vanadic acid  
ethoxydichloride [VO(OEt)Cl<sub>2</sub>] and further 0.04 mmol of  
methyl trichloroacetate as catalyst-activating agent.  
Thus, there was obtained 52 g of a good particulate  
15 copolymer having a particle size of about 2 mm. The  
ethylene content of this rubberlike copolymer was 34%  
by weight. In this invention, there was observed no  
adhesion of copolymer particles to polymerization vessel  
or agitating blades.

### 20 EXAMPLE 4

Copolymerization was conducted in the same manner  
as in Example 1, except that an autoclave made of glass  
was used. Also in this copolymerization, there was  
observed neither mutual adhesion of polymer particles  
25 nor adhesion of polymer particles to vessel walls or  
agitating blades, and the resulting copolymer was good

1 particles having a particle size of about 2 mm. Thus,  
40 g of a copolymer having an ethylene content of 70% by  
weight was obtained.

#### EXAMPLE 5

5           Into the same reactor as used in Example 1 were  
charged 1.2 liters of ethylene dichloride and 40 mg (about  
25 ppm) of sodium dioctyl sulfosuccinate. Thereinto  
were introduced 18 g of ethylene and 60 g of 1-butene,  
after which while maintaining the reactor at 40°C, hydrogen  
10 as a molecular weight regulator was added at a partial  
pressure of 0.4 kg/cm<sup>2</sup> and the copolymerization was  
conducted by continuously adding 1 mmol of ethylaluminum  
sesquichloride, 0.1 mmol of vanadium oxytrichloride and  
0.4 mmol of n-butylperchlorocrotonic acid. During the  
15 copolymerization, 43 g of ethylene and 8 g of 1-butene  
were continuously supplied. After-treatment of the result-  
ing product was carried out in the same manner as in  
Example 1 to obtain 50.6 g of a good rubberlike particulate  
copolymer having a particle size of about 2 mm. The  
20 ethylene content of the copolymer was 85.2% by weight.  
In this copolymerization, there was observed no adhesion  
of copolymer particles to polymerization vessel or  
agitating blades.

#### EXAMPLE 6

25           Copolymerization was conducted in the same manner  
as in Example 5, except that 14 mg of TiCl<sub>4</sub> supported on

1  $\text{MgCl}_2/\text{SiO}_2$  and 2 mmol of triethylaluminum were used as  
catalyst components, that 25 g of ethylene and 80 g of  
propylene were used as initially charged monomers, and  
that during the polymerization, 31 g of ethylene and 10 g  
5 of propylene were continuously supplied. After-treatment  
was carried out in the same manner as in Example 5 to  
obtain 40.3 g of a good rubberlike particulate copolymer  
having a particle size of about 2 mm. The ethylene content  
of the copolymer obtained was 78.3%. In this copolymer-  
10 ization, there was observed no adhesion of copolymer  
particles to polymerization vessel or agitating blades.

#### EXAMPLE 7

Copolymerization was conducted in the same manner  
as in Example 1, except that 2.4 g of 5-ethylidene-2-  
15 norbornene was continuously added in place of the ethylene  
continuously added during the copolymerization. The  
resulting ternary polymer was rubberlike good particles  
having a particle size of about 2 mm. Thus, 39 g of the  
ternary copolymer was obtained. The ethylene content of  
20 the ternary copolymer was 66% by weight as determined by  
infrared absorption spectrum, and its iodine value was 8.

## WHAT IS CLAIMED IS:

1. In a process for producing an ethylene copolymer by copolymerizing ethylene with an  $\alpha$ -olefin or copolymerizing ethylene with an  $\alpha$ -olefin and a non-conjugated diene in the presence of a Ziegler-Natta catalyst comprising an organoaluminum compound and a compound of a transition metal belonging to Group IV or V of the periodic table or comprising these and a catalyst-activating agent, in a polymerization medium which is substantially incapable of dissolving the resulting ethylene copolymer, and thereby producing a rubberlike ethylene copolymer in particulate form, the improvement which comprises adding to polymerization system, as an adhesion-preventing agent, an alkali metal salt of sulfocarboxylic acid dialkyl ester or a composition comprising (a) a polysulfone copolymer of sulfur dioxide and an olefin compound, (b) a polyamine comprising a reaction product of epichlorohydrin with an N-aliphatic hydrocarbylalkylenediamine, and (c) an oil-soluble sulfonic acid.
2. A process according to Claim 1, wherein the alkali metal salt of a sulfocarboxylic acid dialkyl ester is an alkali metal salt of dialkyl sulfosuccinate.
3. A process according to Claim 2, wherein the alkali metal salt of a dialkyl sulfosuccinate is an alkali metal salt of dioctyl sulfosuccinate or dihexyl sulfosuccinate.
4. A process according to Claim 1, wherein the alkali metal salt is a sodium salt or a potassium salt.

5. A process according to Claim 1, wherein the amount of the adhesion-preventing agent is 5 to 100 ppm in the polymerization medium.
6. A process according to Claim 1, wherein the polymerization medium is propylene, propane, 1-butene, butane, methylene chloride, ethylene chloride or ethyl chloride.
7. A process according to Claim 1, wherein the  $\alpha$ -olefin is propylene or 1-butene, and the non-conjugated diene is 1,4-hexadiene, dicyclopentadiene or 5-ethylidene-2-norbornene.
8. A process according to Claim 1, wherein the polymerization temperature is  $-40^{\circ}\text{C}$  to  $60^{\circ}\text{C}$ .
9. A process according to Claim 1, wherein the organoaluminum compound is triethylaluminum, diethylaluminum chloride, diisobutylaluminum chloride, ethylaluminum sesquichloride or ethylaluminum dichloride.
10. A process according to Claim 1, wherein the transition metal compound is vanadium tetrachloride, vanadium oxytrichloride, vanadic acid triethoxide, vanadic acid diethoxychloride, vanadic acid ethoxydichloride, vanadic acid tributoxide, vanadic acid dibutoxychloride, vanadic acid butoxydichloride or vanadium triacetyl-acetonato.
11. A process according to Claim 1, wherein a catalyst-activating agent is present in the polymerization system.
12. A process according to Claim 1, wherein the



catalyst-activating agent is methyl trichloroacetate, butyl perchlorocrotonate, butyl 2,3,4,4-tetrachloro-3-butenate or trichloroacetic acid-ethyl cellosolve ester.

13. A process according to Claim 1, wherein the ethylene content of the ethylene copolymer is 20 to 90% by weight.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	<u>DE-A- 2 535 597</u> (SHOWA DENKO)  * Claims 1,8,10; page 4, paragraph 5 - page 6, paragraph 1; page 10, paragraph 2; page 25, table III; page 27, table IV *  ---	1-13	C 08 F 210/16 C 08 F 4/64 C 08 F 2/00
A	<u>US-A- 3 219 651</u> (R.W. HILL et al.)  * Claims 1, 16 *  ---	1	
A	<u>DE-A- 1 236 200</u> (CHEM. WERKE HULS)  * Claim; column 2, lines 34-46 *  -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 08 F
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 22-10-1985	Examiner DE ROECK
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons  & : member of the same patent family, corresponding document	



### CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claims:
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

### X LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions.

namely:

- 1) Claims 1-13: Adhesion preventing agent = alkali metal salt of a sulfocarboxylic acid dialkyl ester
- 2) Claim 1: Mixture of
  - a) polysulfone
  - b) polyamine
  - c) oil soluble sulfonic acid

- ☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☐ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims: